THE ADSORPTION OF NITROGEN, ACETYLENE, ETHYLENE AND ETHANE ON A SERIES OF ACTIVATED CHARCOALS

by

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EDMONTON, ALBERTA
August, 1958.

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THE UNIVERSITY OF ALBERTA

THE ADSORPTION OF NITROGEN, ACETYLENE, ETHYLENE AND ETHANE ON A SERIES OF ACTIVATED CHARCOALS

A DISSERTATION

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

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by

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ABSTRACT

The Langmuir equation was applied to the adsorption data for nitrogen, acetylene, ethylene and ethane measured at two sets of temperatures near their boiling points. The V_m values calculated from the slopes of the Langmuir plots were used to obtain an estimate of the charcoal surface areas and the molecular adsorption areas of the above gases. The latter values seemed to indicate that the charcoals did not exhibit any difference in the sieving properties with respect to the four gases.

Use was made of the Clausius-Clapeyron equation to calculate the differential heats of adsorption of nitrogen, acetylene, ethylene and ethane on selected samples of the charcoals investigated. The values revealed that the surface affinity of the charcoals for the adsorbates decreased with increasing activation.

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INTRODUCTION

Surface area studies of steam activated charcoals have revealed that the activation process, in increasing the surface area, produces a change in pore size and pore-size distribution. Gas adsorptions involving adsorbate molecules of varied sizes have shown that the less activated charcoals have a larger proportion of fine pores than do the more activated samples (1, 2, 3). Because of the sieving effects by these fine pores, the large adsorbate molecules have access to less internal surface than do the small molecules. Consequently, the surface areas calculated on the basis of the large molecules will be smaller than those based on the small molecules. The screening effect on the large molecules becomes less pronounced on charcoals with larger pores that are produced by longer activation.

In their work on molecular adsorption areas, Nay and Morrison (4) found that the sieving effect of activated charcoals will permit one not only to obtain a qualitative picture of pore-size and pore-size distribution, but it can also be utilized to obtain a quantitative estimate of molecular cross-section dimensions. Accessibility of the adsorbate to the fine pores of the surface was observed to be a function of molecular thickness. This phenomenon permitted a comparison of the thickness of the hydrocarbon gases ranging from acetylene to iso-butane.

The possibility of a relationship between pore size and surface forces is indicated by the variation in the differential heat of adsorption, Q_d, with coverage. Usually, there is a rapid decrease in Q_d with

the small amount adsorbed initially, followed by a less rapid change with continued adsorption (5, 6). This variation is considered to be primarily the result of adsorption tending to occur first in the fine capillaries where both walls may be in contact with the adsorbed molecule, followed by adsorption in pores where the molecule may be attracted by one wall only, or by one wall and the molecule adsorbed on the opposite wall. A contributing factor may be initial adsorption (at low pressures) on surface sites exhibiting greater van der Waals forces of attraction, followed by adsorption on less active points, the surface activity being independent of pore dimensions.

The gas-charcoal adsorption isotherm is concave to the pressure axis with a flattening out in the region of saturation. With increasing temperatures, the isotherm becomes less and less concave. This type of isotherm is thought to represent unimolecular adsorption and has been most successfully interpreted by Langmuir (7).[1] Assuming fixed-site adsorption and negligible molecular interaction in the adsorbed film parallel to the surface, Langmuir derived the equation:

$$v = \frac{V_m bp}{1+bp} \quad \text{or}$$

$$\frac{p}{v} = \frac{1}{bV_m} + \frac{p}{V_m}$$

where V_m is the completed monolayer calculated from the slope of the

---

[1] It may, however, be questioned whether the Langmuir treatment, which is strictly applicable only to non-porous adsorbents such as glass, really expresses the actual events occurring during sorption of vapours on complex, finely-pored solids.

linear plot $\frac{p}{v}$ against p, v is the volume adsorbed at the equilibrium pressure p, and b is a constant relating the rate of condensation to the rate of evaporation. The V_m values obtained for different gases on a given adsorbent can be used to calculate the adsorption areas of the adsorbate molecule and also the surface area of the adsorbent if the molecular adsorption area of the reference gas is known (1, 2, 4). The reference gas most commonly used is nitrogen. To measure the molecular adsorption areas, use is made of the following relationship:

$$a = \frac{V'_m}{V_m} \cdot a'$$

where V'_m = completed monolayer (ml.(n.t.p.)/g.) of the reference gas

V_m = completed monolayer (ml.(n.t.p.)/g.) of the gas investigated

a' = molecular adsorption area of the reference gas in $\mathring{A}^2$

a = molecular adsorption area ($\mathring{A}^2$) of the gas in question

The surface area of the adsorbent is equal to:

$$\frac{V_m \times N \times a \times 10^{-23}}{22.4} \quad \frac{m^2}{gm}$$

where V_m = completed monolayer (ml.(n.t.p.)/g.) of the gas employed to measure the surface area

a = molecular adsorption area of the gas in $\mathring{A}^2$

N = Avogadro's number (6.023×10^{23})

Since V_m varies with temperature, decreasing as the temperature is increased, the choice of a suitable adsorption temperature for surface area and molecular area determinations is very important (8). If the bath temperature is at or near the boiling point of the adsorbate, liquid

packing is assumed, and the surface area of the solid is calculated from the section areas of the adsorbate molecules exhibited in the liquid state.

The differential heat of adsorption, Q_d, is defined as the change in the heat of adsorption resulting from a minute increase in the amount adsorbed and is expressed as kcals. per mole of gas adsorbed. In general, Q_d is a function of the amount adsorbed, the nature of the adsorbent and adsorbate, and the temperature. In physical adsorption it is usually one to two times the latent heat of condensation of the adsorbate in question, indicating that the forces involved in this kind of adsorption are the van der Waal forces operating in condensation. In chemisorption, Q_d is many times greater than the latent heat of condensation and is equivalent to the heats of chemical reaction.

The differential heat of adsorption can be obtained by applying the Clausius-Clapeyron equation to adsorption isotherms measured at two temperatures not too widely separated. According to this equation:

$$- Q_d = \frac{RT_2T_1}{T_2 - T_1} (\ln p_2 - \ln p_1)$$

where p_2 and p_1 are the equilibrium pressures for a fixed amount adsorbed at the temperatures T_2 and T_1 ^{o}K respectively; R is the gas constant (1.98 calories/mole/degree). Gregg (5) emphasizes the necessity of checking the reversibility of adsorption between the two temperatures, T_1 and T_2, since the Clausius-Clapeyron equation is thermodynamic in origin. He also cautions against measuring the isotherms independently since many adsorbents often change slightly with subsequent runs.

The object of this investigation was twofold:

(1) To study the molecular sieve properties of the present series of charcoals with respect to nitrogen, acetylene, ethylene and ethane in the manner reported by Nay and Morrison (4) and by MacCosham (2);

(2) To examine the effects of charcoal activation on the differential heats of adsorption of the same gases.

Nay and Morrison, and MacCosham, assumed a molecular adsorption area of 16.2 $\mathring{A}^2$ for nitrogen, the reference gas. The same value was used here to allow for comparison of the molecular adsorption areas of acetylene, ethylene and ethane.

EXPERIMENTAL

1. Materials

This study was made on a selected number of steam activated charcoals of different activation from a series kindly supplied by the Barnebey-Cheney Company, Columbus, Ohio. The activities used were numbered 1.4, 2.4, 20, 60 and 90, the first two being the least activated. These numbers are times in minutes to breakthrough for the accelerated chloropicrin test in a standard procedure (air containing 0.286 moles per liter of chloropicrin flowing at one litre per minute per square centimeter through a 10 cm. column). Dry weights of the samples were used and ranged from 0.1704 g. for activity 90 to 0.5113 g. for activity 1.4.

Purified grade nitrogen was obtained from Canadian Liquid Air Company; helium (99.8%) and ethylene (99.5%) from the Ohio Chemical Company; acetylene (99.5%) from The Matheson Company; research grade ethane from the Phillips Petroleum Company. The helium and nitrogen were passed through an activated charcoal trap immersed in a liquid nitrogen bath prior to entry into a storage bulb. Acetylene and ethylene were purified further by fractional distillation. The ethane was passed directly into the storage bulb.

Adsorption measurements of these gases were not corrected for deviations from ideality in view of Nay's findings (1).

Dow Corning vacuum grease proved very satisfactory for ordinary stopcocks for all gases except ethane. This gas seemed to dissolve the

grease and contamination with air resulted in about a week after the gas was introduced into the storage bulb. A vacuum stopcock was substituted and no further difficulty was encountered.

2. Apparatus

The apparatus was originally built and used by Nay and Morrison (4) and is similar to the one described by Emmett (9). Minor improvements were made to facilitate operation. A second pump was installed for drawing down the mercury in the gas burette, monometer, and McLeod gauge. It was also used for initial evacuation of the charcoal following an adsorption, the main pump being employed only for the final stages of evacuation. A magnifying lens was attached to the monometer to improve observation of the approach of mercury to the reference pointer and a pair of tweezers was fixed to the monometer stopcock to serve as a lever for careful adjustment of the mercury.

3. Cold Dead Space

The cold dead space of the adsorption bulb was determined with helium at -90°C. The decision to use this temperature was based on the values obtained for a blank adsorption bulb and one with a charcoal sample at the following temperatures (°C): -193.5, -100, -90, -75, -50, -25 and 0. For the blank bulb, there was no indication of a change in cold dead space values with temperature, but those at -50, -25, and 0°C were not as consistent as at the lower temperatures. With the charcoal sample, the value obtained at -193.5°C was slightly higher than at the other temperatures due to the adsorption of helium at this low temperature. There appeared to be no trend for the cold dead space to decrease

with increasing temperature at the higher temperatures, but, as with the blank bulb, the values at -50, -25 and 0°C showed a tendency to fluctuate.

4. Adsorption Temperatures

The boiling points (in brackets) and the temperatures at which the adsorption isotherms were measured are listed below, in °C:

Nitrogen: (-195.8); -193.5, -182.5; -100, -90; -50, -40

Acetylene: (-83.6); -81, -71; 0, +10

Ethylene: (-103.9); -101, -91; -19, -9

Ethane: (-88.3); -86, -76; -5, +5

The data at the two lowest temperatures for each adsorbate were plotted according to the Langmuir equation. The slopes of the linear portions of the isotherms were used to calculate the maximum adsorptions (V_m) of each gas on each charcoal. The differential heats of adsorption were calculated from pairs of empirical isotherms measured at the different sets of low and high temperatures. This was done by applying the Clausius-Clapeyron equation.

Liquid nitrogen and oxygen baths were used for measuring the nitrogen isotherms at -193.5°C and -182.5°C, respectively. Acetone baths were used for all the other isotherm measurements except acetylene at 10°C; in this case a water bath was employed. The temperatures of the baths were brought down with dry ice as near as possible to those at which adsorptions were measured, and then lowered further and maintained at the specified temperatures with liquid nitrogen which was pumped into a 20 cm. test tube immersed in the acetone. The water bath was also

maintained at its temperature of 10°C by a liquid nitrogen finger. The bath temperatures were measured with a Leeds and Northrup potentiometer and a copper-constantan thermocouple to an accuracy of ± .25°C for the acetone and water baths, and ± 0.5°C for the liquid nitrogen and oxygen baths. All baths were continuously stirred.

5. Room Temperature

With the exception of the gas burette which was jacketted by a circulating water bath maintained at 25 ± .02°C, the apparatus was exposed to room temperature kept within a limit of change of ± 0.5°C. The average of the room temperature readings was used in calculations since a set of calculations employing the individual readings did not affect the results. Whenever the temperature occasionally varied more than ± 0.5°C, several averages were used.

6. Charcoal Evacuation

The charcoal samples were initially evacuated at 300°C for 3 hours and at 300° for 30 minutes after each adsorption. The highest vacuum of 10^{-3} microns was obtained at this temperature and in these periods of time.

7. Reproducibility of Isotherms

Most of the adsorption isotherms at the two sets of lowest temperatures were measured in duplicate. With few exceptions, only one isotherm was measured at each of the higher temperatures because of the time limitation. Very good reproducibility was obtained for the majority of duplicate runs as seen for ethane at -80°C on charcoal 20 (Figure 2) and ethane on charcoal 2.4 at -5°C. Repeat determinations

were sometimes encountered which differed by approximately 0.2% in the total volume adsorbed. This variation was attributed to an error in setting the potentiometer for temperature measurement. Calculations from the non-coincident isotherms were averaged.

8. Equilibrium Times

For all adsorbates on each charcoal, adsorption appeared to be nearly complete within 10 to 15 minutes at the lower temperatures, and within 5 to 10 minutes at the higher temperatures. For the initial steps of several isotherms, no further appreciable changes in pressure could be detected in consecutive readings over an additional period of time ranging from 20 minutes to more than 2 hours. For example, the pressures for ethane (-86°C) on charcoal 2.4 were 7.42 cms. and 7.40 cms. at 10 and 30 minutes respectively, the initial pressure having been 39.58 cms. For acetylene at 0°C, the initial pressure was 9.30 cms., at the end of 6 minutes it was 3.60 cms., and after $2\frac{1}{2}$ hours it was 3.59 cms. This, however, should not be taken as an indication that true equilibrium is attained. It is probable that slow adsorption continued after diffusion of the molecules through the finest pores (4), but the magnitude of this effect appears likely to be so small as to leave the results reported below substantially unaffected.

This conclusion is reinforced by measurements of desorption points for selected isotherms on charcoals 1.4 and 20. Approximately 10 to 15 minutes were allowed for each adsorption and desorption step. The plots obtained for acetylene at -81°C on charcoal 20 and ethane at -5°C on charcoal 1.4 are shown in Figures 1 and 2. The desorption

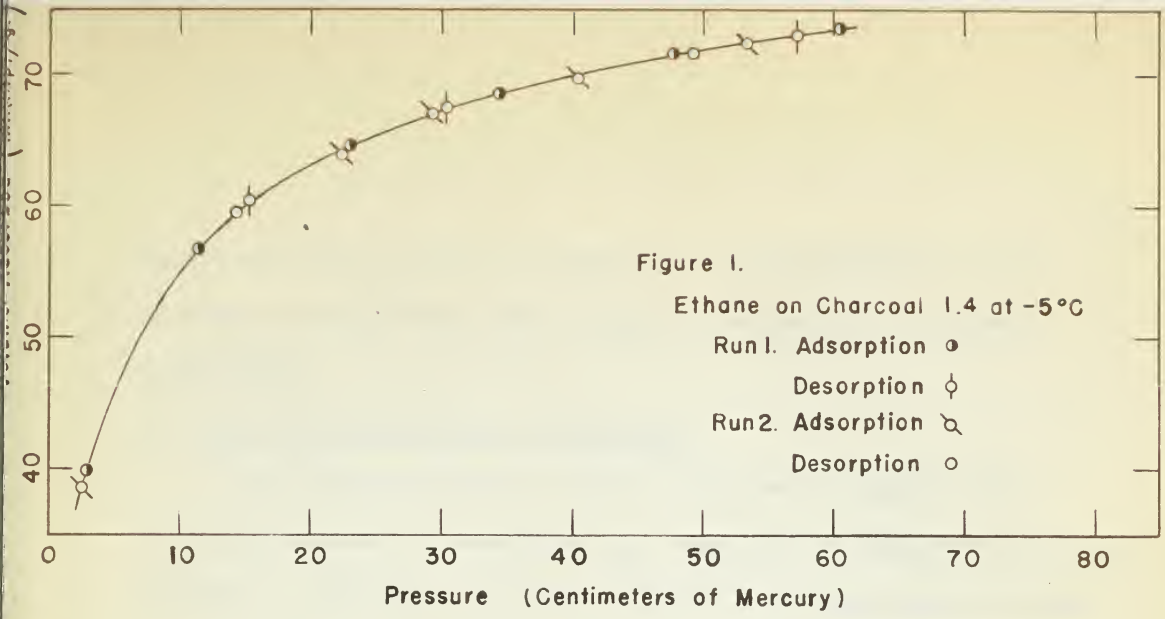


Figure 1.
Ethane on Charcoal 1.4 at -5°C
Run 1. Adsorption ◑
Desorption ◊
Run 2. Adsorption ⊘
Desorption ○

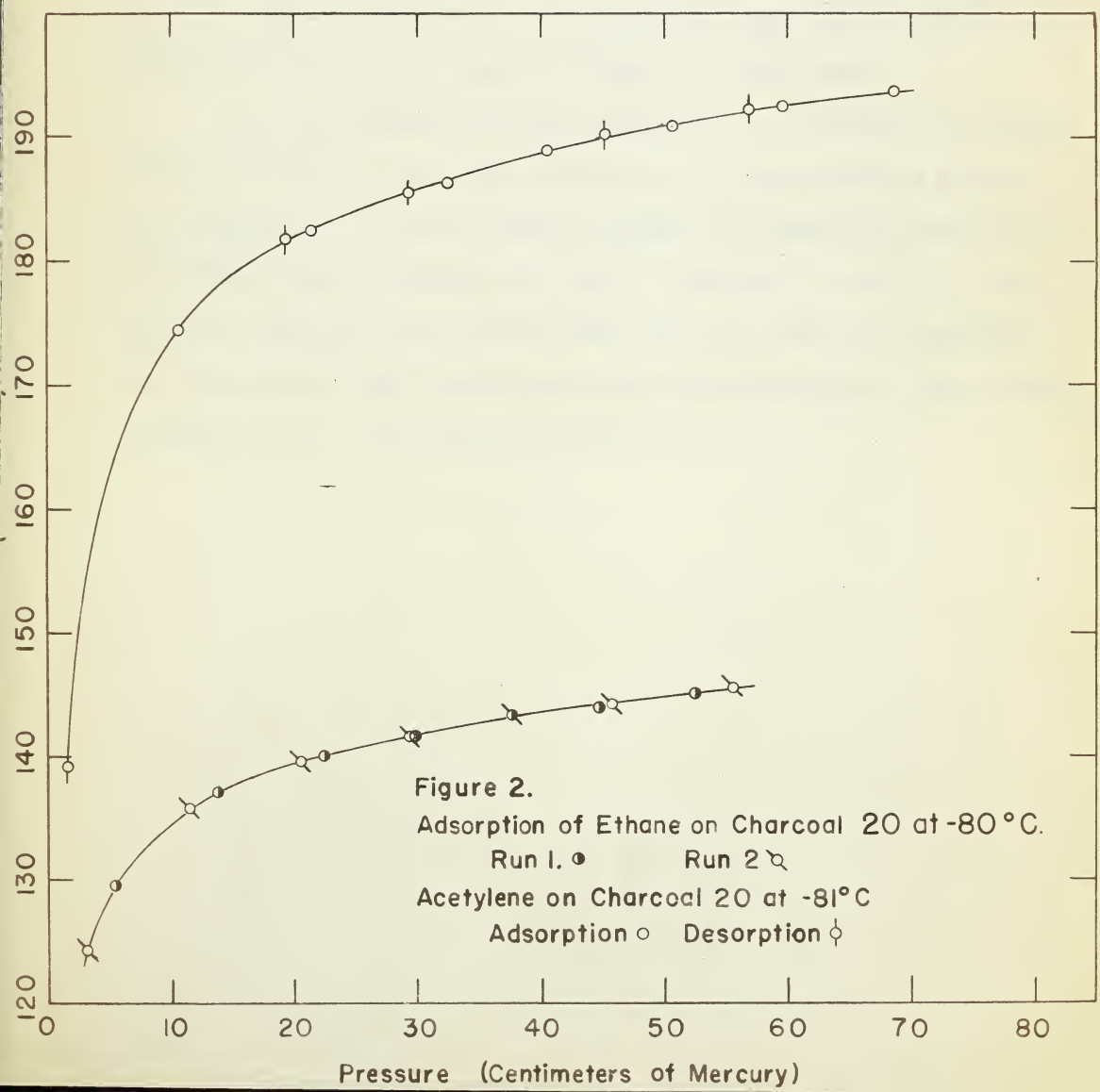


Figure 2.
Adsorption of Ethane on Charcoal 20 at -80 °C.
Run 1. ◑ Run 2 ⊘
Acetylene on Charcoal 20 at -81°C
Adsorption ○ Desorption ◊

points are seen to fall on the same line as the adsorption points. Nitrogen at -193.5°C and -40°C (Figure 4) on charcoal 1.4 behaved identically.

9. The Differential Heats of Adsorption

The Clausius-Clapeyron equation was used to calculate the differential heats of adsorption, Q_d, from pairs of adsorption isotherms measured at temperature intervals of 10°C in all cases except nitrogen near its boiling point, where the temperature range varied from 10 to 11 degrees depending on the liquid nitrogen and oxygen baths.

Since the Clausius-Clapeyron equation is thermodynamic in origin, it was necessary to check the reversibility of the adsorption process with temperature. This was done by raising the temperature from T_1 to T_2 during a given adsorption step and the lowering it back to T_1, the pressure returned to its initial value indicating that the adsorption was reversible. This, together with the reproducibility of the isotherms, justified use of the Clausius-Clapeyron equation.

RESULTS

Application of the Langmuir equation to the adsorption data obtained resulted in the two types of plots seen in Figure 3. The plot for ethane on charcoal 2.4 is representative of all the isotherms for charcoals 1.4, 2.4, 20 and 60; that for acetylene is typical of the charcoal 90 isotherms. The completed monolayer volumes (V_m) calculated from the slopes of the Langmuir plots are listed in Table I. These values were used to calculate the molecular adsorption areas of acetylene, ethylene and ethane (Table II) and the charcoal surface areas (Table III).

The differential heats of adsorption are seen in Tables V, VI, VII and VIII.

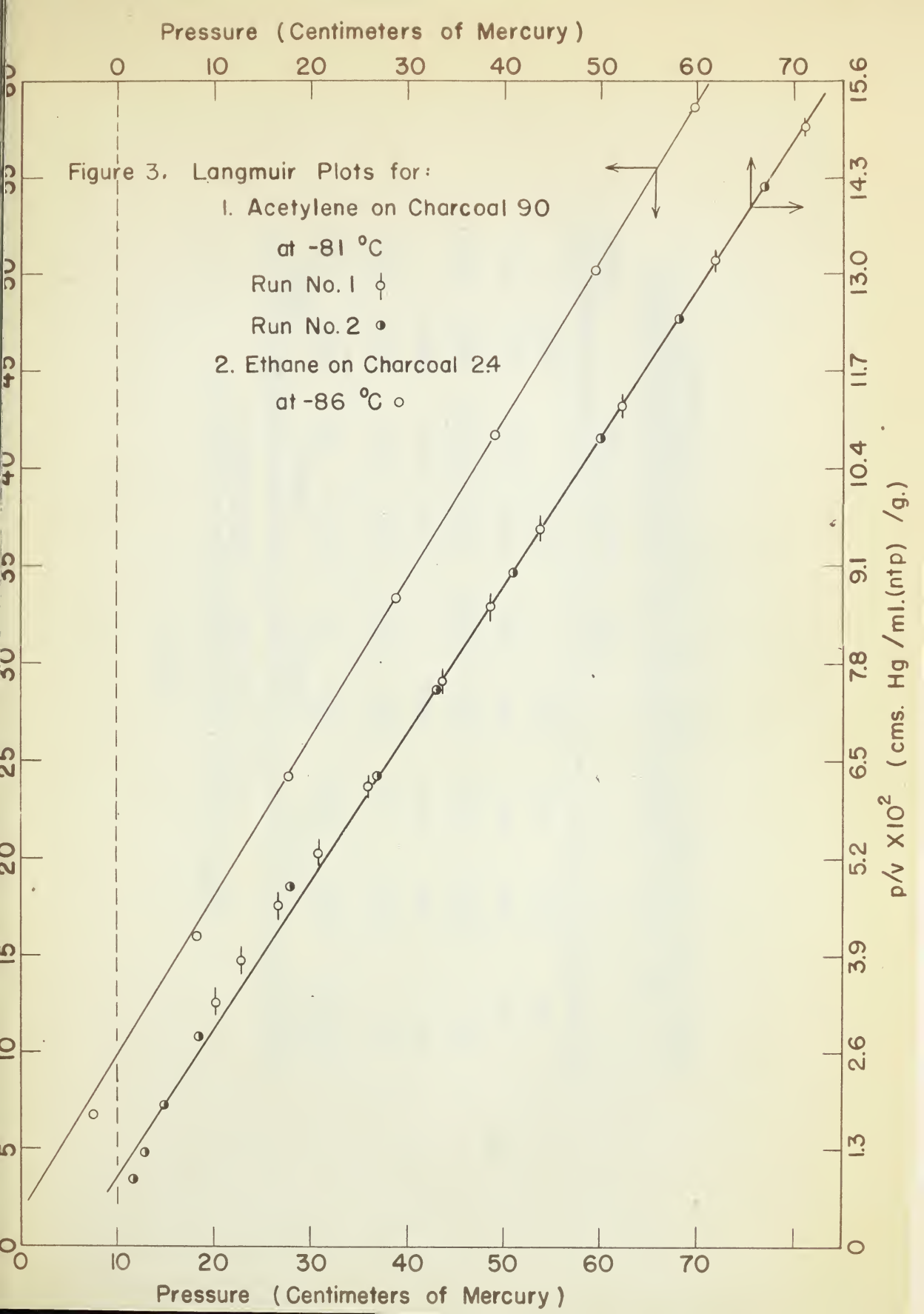

Pressure (Centimeters of Mercury)
0
10
20
30
40
50
60
70
Figure 3. Langmuir Plots for:
1. Acetylene on Charcoal 90
at -81 °C
Run No. 1
Run No. 2
2. Ethane on Charcoal 24
at -86 °C
p/v X10² (cms. Hg /ml.(ntp) /g.)
0
1.3
2.6
3.9
5.2
6.5
7.8
9.1
10.4
11.7
13.0
14.3
15.6
Pressure (Centimeters of Mercury)

TABLE I

MAXIMUM ADSORPTION (V_m) OF GASES IN ml.(n.t.p.)/g. OF CHARCOAL AT TWO SETS OF TEMPERATURES °C

Charcoal	Nitrogen		Acetylene		Ethylene		Ethane	
Activity	-193.5	-182.5	-81	-71	-101	-91	-86	-76
90	626.6	(1)	505.8	495.7	436.7	421.6	387.6	372.6
60	374.6	359.9	299.0		258.3	250.9	228.7	
20	251.4	239.2	199.3	191.0*	174.2*	168.4*	152.4	148.6*
2.4	203.4	194.6	161.3	156.2	141.5	136.3	122.2	119.4
1.4	180.3	174.1	144.8		127.2		108.2	
				*-70°C	*-103°C	*-94°C		*-80°C

(1) Curvature of Langmuir Isotherm at this temperature greatly increased (Figure 6). Linear portions selected from two different isotherms presented V_m values of 660.2 and 641.0 cc. Reasons for these values to be discussed.

TABLE II

EFFECTIVE MOLECULAR ADSORPTION AREAS IN $\mathring{A}^2$
BASED ON NITROGEN AT -193°C

Charcoal Activity	Acetylene -81	Acetylene -71	Ethylene -101	Ethylene -91	Ethane -86	Ethane -76
90	20.1	20.5	23.2	24.1	26.2	27.2
60	20.3		23.5	24.2	26.5	
20	20.4	21.3*	23.4*	24.2*	26.7	27.4*
2.4	20.4	21.1	23.3	24.2	27.0	27.6
1.4	20.2		23.0		27.0	
Average	20.3	21.0	23.3	24.2	26.7	27.4
		*-70°C	*-103°C	*-94°C		*-80°C

TABLE III

SURFACE AREAS OF CHARCOALS IN SQUARE METERS PER GRAM

Charcoal Activity	Adsorbate			
	Nitrogen	Acetylene	Ethylene	Ethane
90	2730	2762	2737	2784
60	1632	1633	1619	1642
20	1096	1088	1092	1094
2.4	886	881	887	878
1.4	786	791	797	777

DISCUSSION

1. Molecular Adsorption Areas

In their work on a different series of charcoals, Nay and Morrison observed that accessibility of gas molecules to the internal surface is governed by molecular thickness (4). Compared to nitrogen, the reference molecule, acetylene and ethylene were found to be thinner and capable of entering pores that excluded nitrogen. Ethane was shown to be about as thick as nitrogen, and hence, screening by the finer pores of these two gases was similar. The data they obtained are listed in Table IV and illustrates the effects of sieving on molecular area determinations. Charcoal activity is represented by the charcoal number and average areas are based on the underlined values. The temperatures at which the isotherms were measured are listed below the table.

TABLE IV

MOLECULAR ADSORPTION AREAS OF GAS MOLECULES IN SQUARE ANGSTROMS

Adsorbate	Charcoal Number 1	2	3	4	5	6	7	8	Av.
C_2H_2	15.0	18.1	18.8	19.5	19.3	20.0	19.8	20.2	19.8
C_2H_4	20.4	21.5	22.1	22.5	23.0	23.4	23.2	23.6	23.1
C_2H_6	25.1	25.6	25.8	25.7	26.2	26.1	25.7	26.7	25.9

Adsorption temperatures: Nitrogen -190°C
Acetylene -75.2°C
Ethylene -90.2°C
Ethane -78.2°C

It is seen that for molecules thinner than nitrogen, the molecular areas eventually decreased with less activation of the charcoals. This is due to the relatively smaller adsorption of the reference gas. In the case of the least activated samples the sieving was so pronounced that the calculated area of the acetylene molecule was smaller than the reference value of nitrogen.

Selected samples from the present series of charcoals, including the two of least activation, were investigated in this work, but proved to be too highly activated to produce the changes in molecular adsorption areas observed by Nay and Morrison. The values in Table II show that nitrogen, acetylene, ethylene and ethane probably have equal access to the internal surface of each charcoal. The average areas obtained here compare very well with those listed in Table IV.

In a similar investigation, MacCosham (2) also observed a variation in the molecular adsorption area of acetylene. His average value, however, is considerably greater (22.3 $\mathring{A}^2$) than the area listed by Nay and Morrison. This may be mainly attributed to the higher adsorption temperature employed for acetylene by MacCosham; -61°C compared with -75°C, since the nitrogen bath (-190°C) and the reference value of nitrogen (16.2 $\mathring{A}^2$) were the same. The effect of temperature on molecular area measurements, using the same adsorption temperature and reference value for nitrogen is seen in Table II.

Nay and Morrison, and MacCosham found it necessary to employ the higher adsorption temperatures to avoid capillary condensation with their charcoals. For the present series, on the basis of a preliminary

investigation into the behavior of the Langmuir isotherm and change of V_m with temperature, the adsorptions could have been measured at the boiling points of the adsorbate. However, because the average temperature of liquid nitrogen was -193.5°C, the baths selected for the hydrocarbons were also approximately two degrees above their boiling points to assure better results. If capillary condensation did occur at these temperatures any decrease or elimination of it by using temperatures even slightly higher than those of Nay and Morrison did not change the monolayer values appreciably (Table I).

2. Surface Areas

The surface areas in Table III were calculated from the individual monolayer values and the assumed adsorption area of nitrogen and the average areas of the hydrocarbons. For charcoals 60 and 90 they are considerably greater than the largest areas of the samples examined by MacCosham (2), the area of charcoal 90 being more than twice as large. In MacCosham's work, the highest activated charcoal appeared to be over-activated and its surface area was slightly less than of the sample preceding it. The high value for charcoal 90 here, indicates the effectiveness of the activation process of this series.

Because the small pores at pressures below the saturation pressure are probably full, the values in Table III may represent the relative adsorptive capacities rather than the absolute surface areas of the charcoals.

3. Differential Heats of Adsorption

The differential heats of adsorption, Q_d, were calculated for all

TABLE V

THE DIFFERENTIAL HEATS OF ADSORPTION ON CHARCOAL 90

Adsorbate	T_1 and T_2 °C	Volume (V) Adsorbed ml.(n.t.p.)/g.	$\frac{V}{V_m}$	$-Q_d$ kcal/mol
Nitrogen	-193.5 and -182.5	525.0	.83	1.9
		500.0		1.9
		475.0		1.9
		462.5	.73	1.9
	-100 and -90	80.0	.13	3.1
		70.0		3.2
		60.0		3.3
		50.0	.079	3.3
	-50 and -40	23.0	.036	3.3
		17.0		3.3
		13.0		3.4
		9.0	.014	3.5
Acetylene	-81 and -71	445.0	.88	6.1
		430.0		5.5
		415.0		5.3
		400.0		5.2
		385.0		5.2
		370.0		5.3
		355.0	.70	5.3
	0 and 10	100.0	.20	5.4
		90.0		5.6
		80.0		5.5
		60.0		5.7
		40.0	.079	5.7

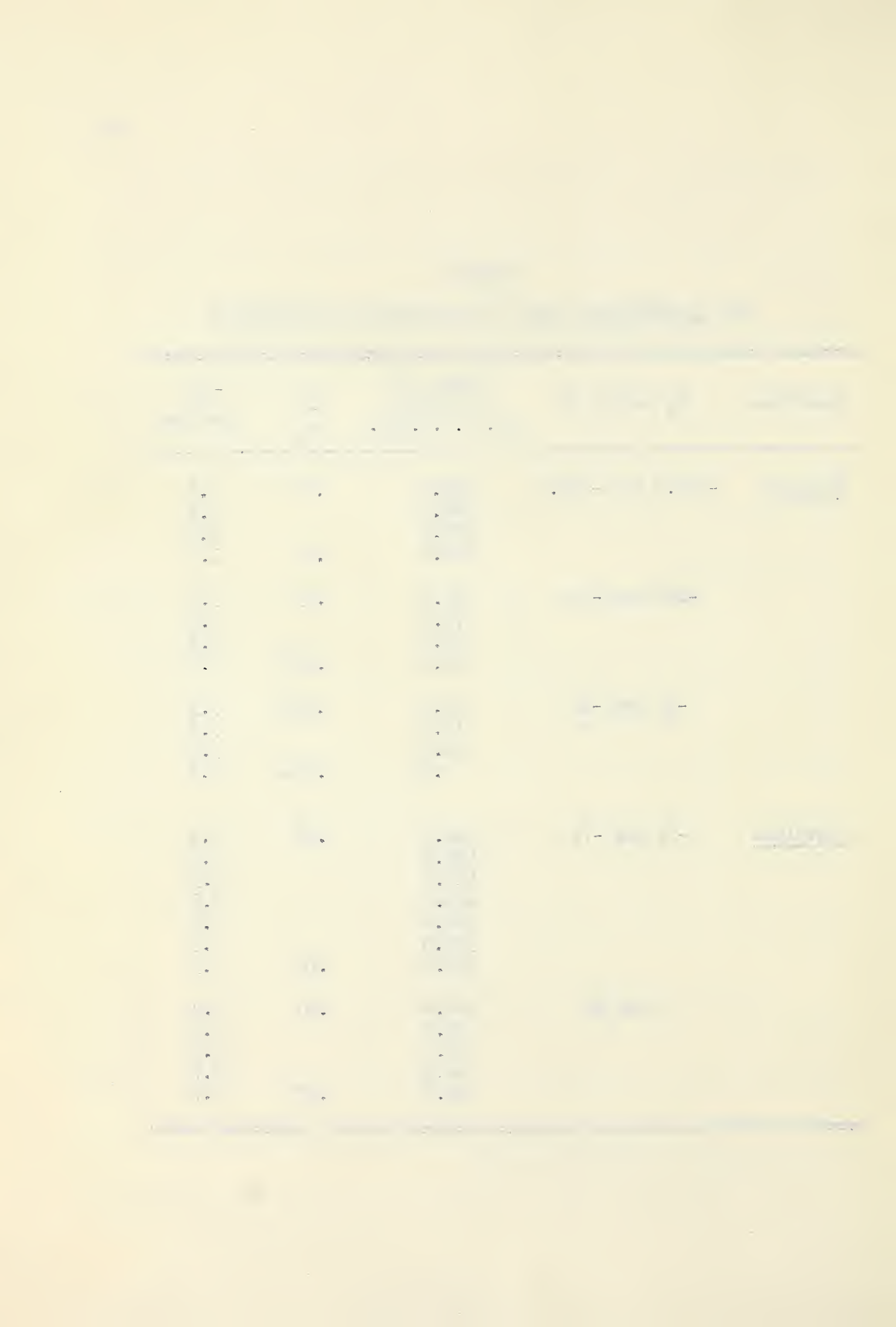


TABLE V (continued)

Adsorbate	T_1 and T_2 °C	Volume (V) Adsorbed ml.(n.t.p.)/g.	$\frac{V}{V_m}$	$-Q_d$ kcal/mol
Ethylene	-101 and -91	392.0	.88	5.6
		380.0		5.0
		365.0		4.8
		350.0		4.7
		335.0		4.7
		320.0	.72	4.7
	-19 and -9	137.5	.31	5.5
		112.5		5.4
		87.5	.20-	5.5
Ethane	-86 and -76	350.0	.89	6.5
		344.0		6.3
		335.0		5.7
		329.0		5.5
		320.0		5.4
		314.0		5.5
		305.0	.78	5.4
	-5 and 5	135.0	.34	5.8
		120.0		5.8
		100.0	.25	5.8

TABLE VI

THE DIFFERENTIAL HEATS OF ADSORPTION ON CHARCOAL 60

Adsorbate	T_1 and T_2 °C	Volume (V) Adsorbed ml.(n.t.p.)/g.	$\frac{V}{V_m}$	$-Q_d$ kcal/mol
Nitrogen	-193.5 and -182.5	334.0	.88	2.3
		328.0		2.3
		320.0	.84	2.2
	-50 and -40	24.0	.063	3.6
		20.0		3.7
		15.0	.039	3.8
Ethylene	-101 and -91	238.0	.92	6.0
		232.0		6.0
		228.0	.88	5.8
	-19 and -9	110.0	.42	5.8
		100.0		6.0
		90.0	.35	6.1

TABLE VII

THE DIFFERENTIAL HEATS OF ADSORPTION ON CHARCOAL 2.4

Adsorbate	T_1 and T_2 °C	Volume (V) Adsorbed ml.(n.t.p.)/g.	$\frac{V}{V_m}$	- Qd kcal/mol
Nitrogen	-193 and -182.5	188.8	.93	2.8
		186.0	.91	2.8
	-100 and -90	70.0	.34	3.6
		60.0		3.7
		50.0	.24	3.7
	-50 and -40	20.0	.098	4.0
		16.0		4.1
		12.0		4.2
		8.0	.039	4.4
Acetylene	-81 and -71	149.2	.92	6.8
		146.0		6.8
		142.0	.88	6.8
	0 and 10	80.0	.50	6.8
		75.0		6.8
		65.0		6.7
		55.0		6.8
		45.0		6.7
		35.0	.22	6.7

TABLE VII (continued)

Adsorbate	T_1 and T_2 °C	Volume (V) Adsorbed ml.(n.t.p.)/g.	$\frac{V}{V_m}$	- Qd kcal/mol
Ethylene	-101 and -91	132.8	.94	6.7
		132.0		6.6
		130.0	.92	6.7
	-19 and -9	84.0	.59	6.8
		77.5		6.9
		70.0	.50	7.2
Ethane	-86 and -76	114.8	.94	7.0
		110.0	.90	6.8
	-5 and 5	78.0	.64	7.4
		75.0		7.2
		70.0		7.2
		65.0	.53	7.0

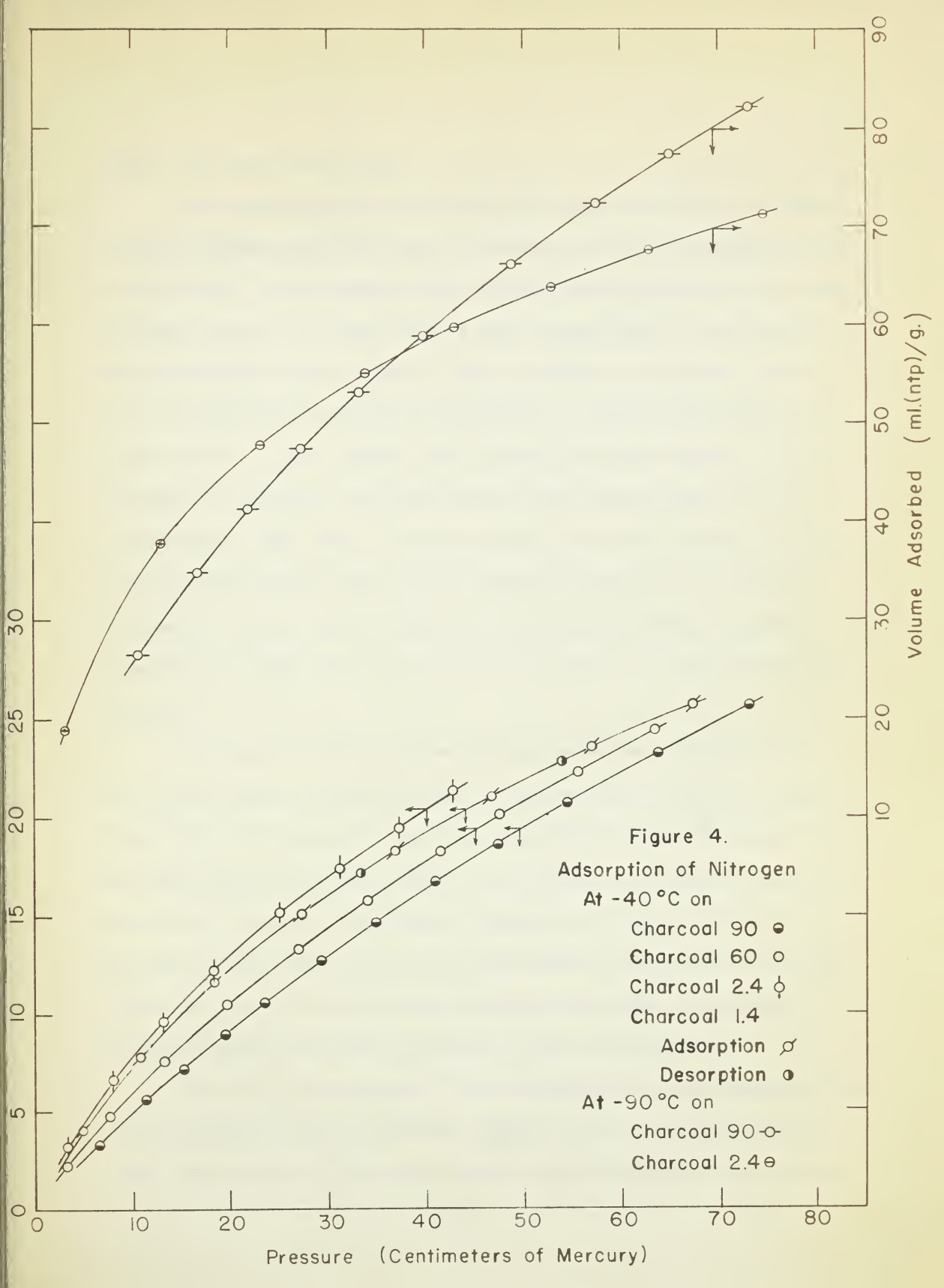
TABLE VIII

THE DIFFERENTIAL HEATS OF ADSORPTION ON CHARCOAL 1.4

Adsorbate	T_1 and T_2 °C	Volume (V) Adsorbed ml.(n.t.p.)/g.	$\frac{V}{V_m}$	$-Q_d$ kcal/mol
Nitrogen	-193.5 and -182.5	167.0	.93	2.7
		164.0	.91	2.8
	-50 and -40	25.0	.14	3.9
		20.0		4.0
		15.0		4.1
		12.5	.069	4.0

gases on charcoals 2.4 and 90, for nitrogen and ethylene on activity 60 and nitrogen only on activity 1.4. The results are listed in Tables V, VI, VII, and VIII, and clearly demonstrate the effect of activation on surface affinity for adsorbate molecules. For all gases at the different temperature ranges, the Q_d values on charcoal 2.4 (Table VII) are higher than those on charcoal 90 (Table V). On activity 60 (Table VI), the nitrogen and ethylene values are seen to be lower than on 2.4, but higher than on 90; here, however, the differences are close to the limits of experimental error. The values for nitrogen on samples 1.4 (Table VIII) and 2.4 are equal. This decrease in surface affinity with increased charcoal activation also is shown in the nitrogen adsorption isotherms at the higher temperatures (Figure 4). At -40°C the less activated charcoals adsorbed a greater volume throughout for the range of pressures employed indicating that at this temperature the surface forces rather than areas are the determining factor. At -100°C the isotherms cross over at the point where surface area becomes the deciding variable.

These findings are in agreement with the work done by Morrison (10) and Habgood and Hanlan (11) on the same charcoal series. The latter conducted a chromatographic study using nitrogen and the simple hydrocarbon gases; they observed that the retention volume and initial heats of adsorption of all gases decreased with increasing activity (i.e., surface) of the charcoal. The water isotherms measured by Morrison showed that a greater volume was initially adsorbed by charcoal 1.4 than 90, but at saturation the total volume adsorbed by the former


Volume Adsorbed (ml.(ntp)/g.)
Pressure (Centimeters of Mercury)
0
10
20
30
40
50
60
70
80
90
5
15
25
Figure 4.
Adsorption of Nitrogen
At -40 °C on
Charcoal 90
Charcoal 60
Charcoal 2.4
Charcoal 1.4
Adsorption
Desorption
At -90 °C on
Charcoal 90
Charcoal 2.4

sample was considerably less.

Since pore dimensions increase with longer activation, the above behavior suggests that the sites of greatest affinity are located in the finest pores. In such pores, both walls may be in contact with the same adsorbed molecule and hence hold it more strongly than if the molecule were adsorbed by only one side. From his studies on graphite, Barrer (12) concluded that the heat of adsorption in a fine crack would be twice that on a plane surface. The highest and lowest values of Q_d recorded for nitrogen, argon and hydrogen were approximately in the ratio of 2:1. This ratio is also approached here with nitrogen on the most activated sample where the two limiting values are 3.5 and 1.9 kcal/mole. In the case of charcoal, a large pore, several molecular diameters in width, would be comparable in effect to a plane surface on graphite.

Although the heats of adsorption for nitrogen on charcoals 1.4 and 2.4 are equal, a greater volume is adsorbed by the latter at -40°C (Figure 4). This suggests that there is probably little enlargement of the pores during the early stages of activation, and mainly a removal of contaminants (wholly or partially) blocking the pores. If this is so, one would expect that for the first few members of the present charcoal series there would be little or no change in the heats of adsorption with activation even though the surface area is increased.

Regarding the variation of the differential heat of adsorption on a heterogeneous surface, the usual behavior is one characterized by a rapid drop in Q_d with the amount adsorbed initially followed by a less

rapid decrease or an approach to a constant value asymtotically (5, 6, 12, 13). This variation is attributed to adsorption occurring first on areas of highest attractive forces and subsequently on less active parts of the surface. There are, however, numerous examples where the region of less rapid change is interrupted by an increase to a maximum, followed again by a decrease (13, 14).

Because the object here was to examine the variation of Q_d with charcoal activation and not surface of a given sample, results are not available for considerable fractions of each charcoal surface. In view of this and the two types of variation in Q_d with coverage, it is not possible to conclude what the behavior is over the entire surface for these charcoals. However, significant features do show up. For the low and high regions of coverage on charcoal 2.4, Q_d for acetylene is constant, but for nitrogen in the same areas, a considerable difference occurs. It was mentioned earlier that the heat of adsorption of a molecule should vary with pore structure. It seems reasonable to conclude, therefore, that with adsorbates of different molecular dimensions a modification may occur in the variation of Q_d with the amount adsorbed. If orientation of the molecule is horizontal, as it is here (4), molecular thickness will be an important factor. Acetylene is a thinner molecule than nitrogen and hence there may be a difference in distribution of the possible arrangements of molecules relative to the opposite pore walls. A more definite conclusion would have been possible if values for ethylene and ethane were available at lower adsorptions since ethane is approximately of the same thickness as nitrogen, whereas

ethylene is thinner.

The sudden drop in Q_d, usually observed with initial adsorption, (5, 6, 12, 13), was not found for any of the charcoals. In the case of the hydrocarbons, the measurements were made at too high a coverage. As for the nitrogen values, they suggest a less rapid initial change with decreasing charcoal activation. The differential heats of adsorption for nitrogen on graphite measured by Barrer (12) fell from 4.55 to 3.74 kcals/mole corresponding to an adsorption from 0.10 to 1.60 ml.(n.t.p.) and then decreased to 2.50 kcals at 80 ml. The drop from 4.4 to 3.6 kcals/mole for nitrogen on charcoal 2.4 for a coverage ranging from 8 to 70 ml.(n.t.p.) (Table VII) seems to indicate that a large fraction of the capillaries in this charcoal are approximately one to two nitrogen diameters in width.

An unusual variation in Q_d occurred with the hydrocarbons on sample 90. In all three cases there was a significant increase at highest coverage; this may be the beginning of a maximum region mentioned earlier and may be due to a phase change in the adsorbed film occurring at the higher pressures.

4. Selective Adsorption

As a surface approaches saturation, the volume it adsorbs is governed by molecular size of the adsorbate. At lower coverage, however, the deciding factor is molecular affinity for the adsorbent (15).

In the case of the charcoals examined in the present studies, preferential adsorption of the hydrocarbons is indicated by Figure 5, but it should be noted that since the heats of adsorption of the

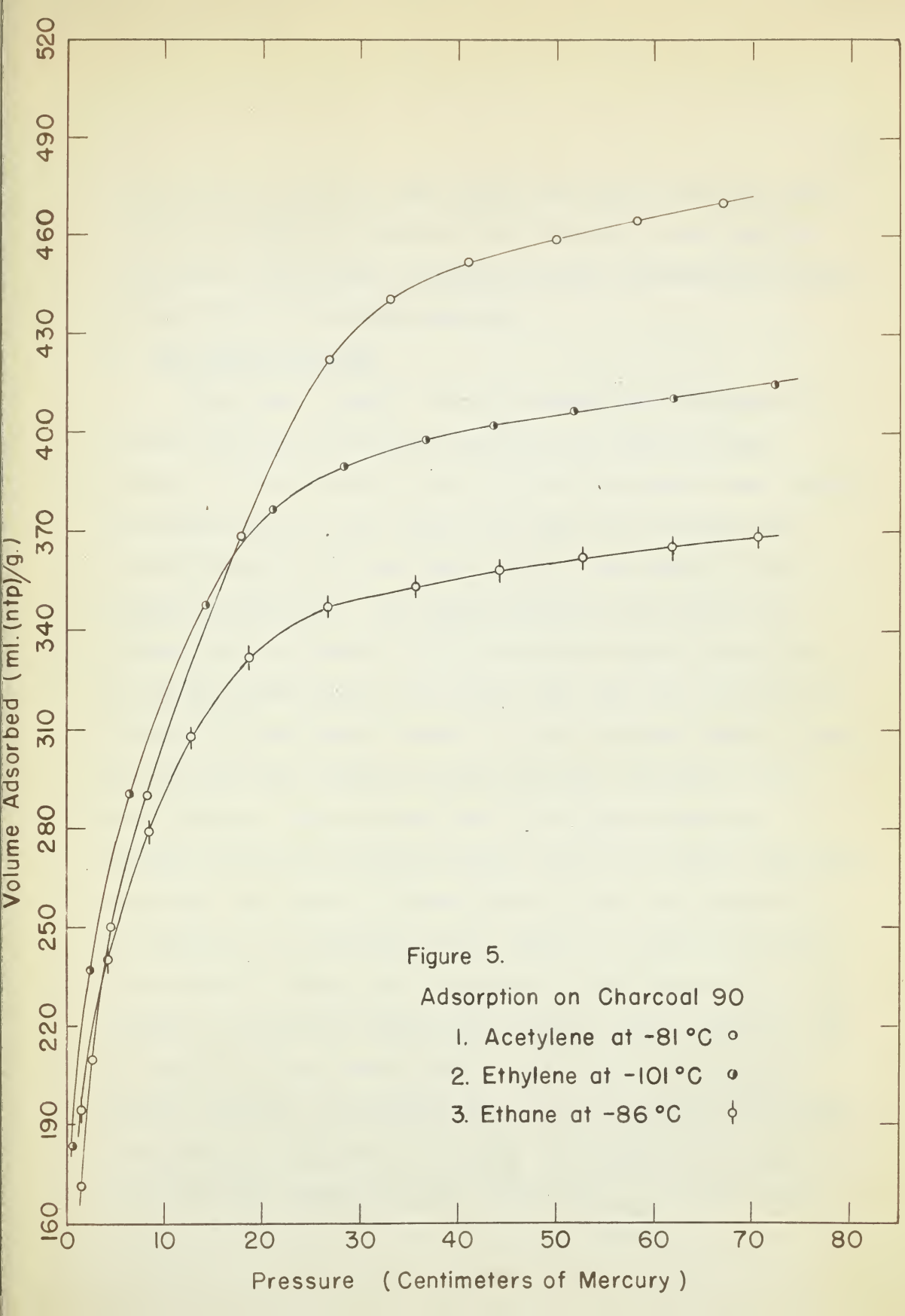


Figure 5.

Adsorption on Charcoal 90

1. Acetylene at -81 °C
2. Ethylene at -101 °C
3. Ethane at -86 °C

hydrocarbons are about the same (Tables V and VII) the initially lower sorption of acetylene by charcoal 90 may arise from a more tenacious adsorption of this gas and a consequent partial (and transient) blocking of fine pores by the adsorbed molecules.

5. The Langmuir Isotherms

It was seen in Figure 3 that the Langmuir plot for charcoal 90 differed from that of the other charcoals in the region of lower pressure. For activities 1.4, 2.4, 20 and 60 the points of each isotherm fell below the line in this region; for sample 90, the points were initially below but then rose above to form a curve concave to the extended linear portion. This unusual behavior of the charcoal 90 isotherm can be attributed to the lower surface forces of attraction. The initial volume changes with pressure were less than if the heats of adsorption had been equal to those of the less activated samples. Hence, the p/v values were relatively higher and caused the points to rise above the line. The cumulative effect of successive adsorptions resulted in the plot eventually becoming linear as the surface approached saturation. The extent of curvature above the line was influenced by the affinity of the adsorbate for the charcoal. As would be expected, it was least for ethane, more for ethylene and most for acetylene. For nitrogen at -193.5°C the behavior was similar to that for ethylene, but at -182.5°C the linear portion did not occur at all. The effect of charcoal activation and adsorbate affinity on the relative volume change with pressure is illustrated in Table IX. The ratios of the volume (ml.(n.t.p.)/g.) adsorbed at 10 cm. pressure ($V_{10\ cm.}$) to the volume

(ml.(n.t.p.)/g.) adsorbed at 60 cm. pressure ($V_{60\ cm.}$) for charcoals 90 and 20 at the lowest temperatures are given.

TABLE IX

RATIO OF $V_{10\ cm.}$ (ml.(n.t.p.)/g.) : $V_{60\ cm.}$ (ml.(n.t.p.)/g.)

Charcoal Activity	Nitrogen -193.5°C	Acetylene -81°C	Ethylene -101°C	Ethane -86°C
90	.79	.66	.78	.79
20	.96	.90	.94	.93

Although, initially, the isotherm for charcoal 90 differed from those for the less activated samples, linearity of all at the lowest temperature began at about 20 - 35 cm. pressure. At the temperature 10° higher linearity for the less activated charcoals appeared to begin at a slightly higher pressure, but for charcoal 90 it came into effect at a much greater pressure. In the case of acetylene, it was 55 - 65 cms. pressure (Figure 6); for ethylene and ethane, 40 - 50 cm. Although a straight line was drawn through the final five points of the nitrogen isotherm at -182.5°C (Figure 6), the value for V_m, 660.2 ml.(n.t.p.)/g., was greater than that obtained from the lower temperature plot, 626.6 ml.(n.t.p.)/g. This indicates that the monolayer volume was calculated from a region similar to the one shown by the dotted line for acetylene at -71°C (Figure 6). From the slope of this line, V_m is 584.6 ml.(n.t.p.)/g. compared to 505.8 ml.(n.t.p.)/g. calculated from the Langmuir plot at -81°C. Because the plots of p/v against p were linear

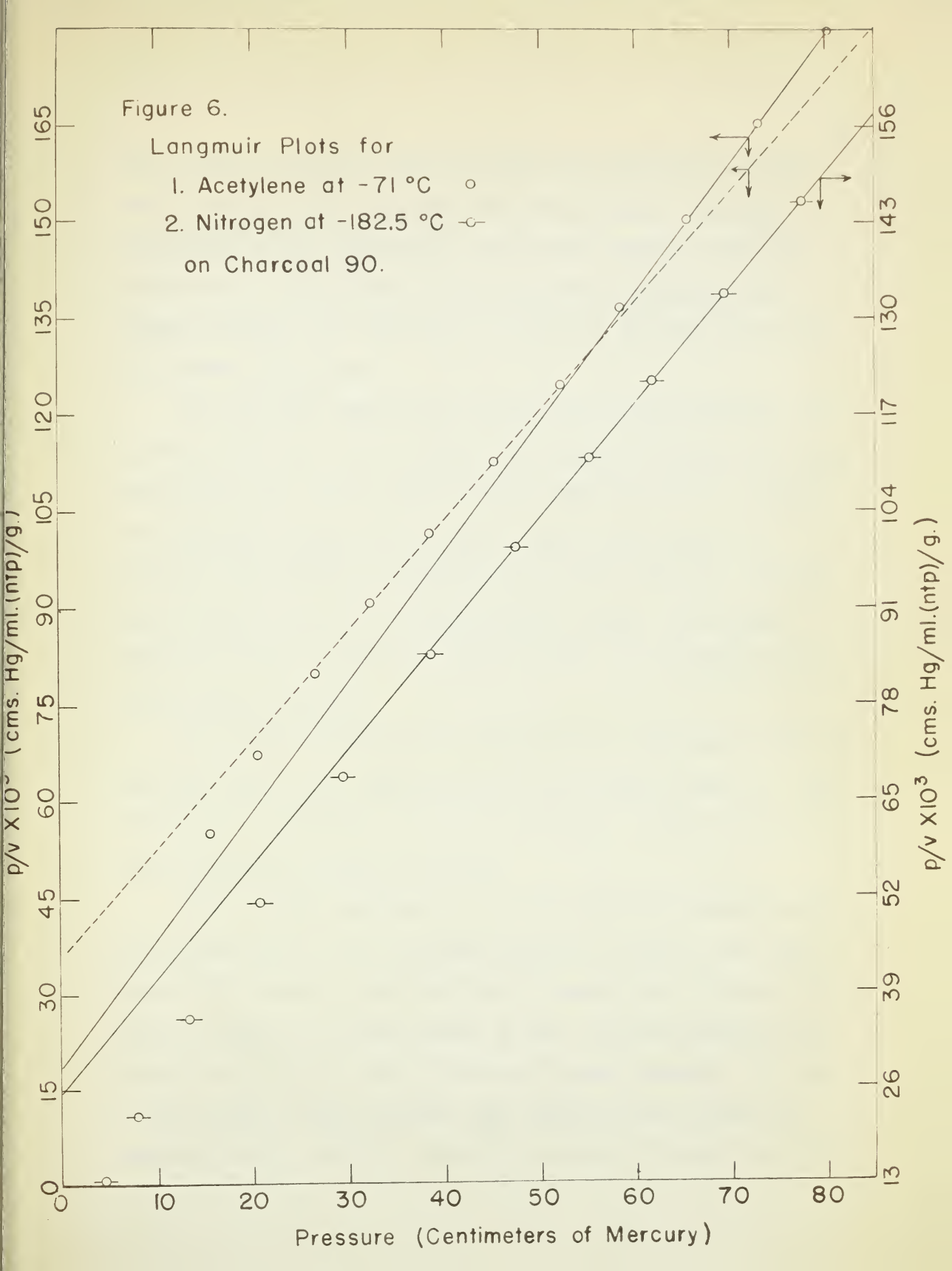


Figure 6.
Langmuir Plots for
1. Acetylene at -71 °C
2. Nitrogen at -182.5 °C
on Charcoal 90.
p/v X10³ (cms. Hg/ml.(ntp)/g.)
p/v X10³ (cms. Hg/ml.(ntp)/g.)
Pressure (Centimeters of Mercury)
0
15
30
45
60
75
90
105
120
135
150
165
13
26
39
52
65
78
91
104
117
130
143
156
10
20
30
40
50
60
70
80

over a range of pressures where the surface was practically saturated and the volume adsorbed increased little with pressure, the lowest temperature data for charcoals 2.4 and 90 were analyzed to see what fraction of the total volume of each gas adsorbed was obeying the Langmuir equation. For charcoal 2.4 it was less than five percent; for 90, less than ten percent.

At the lowest temperature, for the less activated charcoals, the V_m values calculated from the slope of the Langmuir isotherm were only a few ml.(n.t.p.)/g. higher than the volumes adsorbed at 60 cm. pressure. The differences between the two sets of values varied from 2 - 9 ml.(n.t.p.)/g. depending on adsorbate and charcoal activity. For charcoal 90 the V_m's were 27 to 36 ml.(s.t.p.)/g. higher. The volumes adsorbed at 60 cm. pressure are listed in Table X for comparison with the V_m values in Table I.

The greater differences for charcoal 90 are reasonable in view of the final slopes of the empirical plots for nitrogen in Figure 7. They indicate that considerably more can be adsorbed by charcoal 90 than 2.4 before saturation pressure is reached.

Most isotherm measurements on the less activated charcoals near the boiling points of the adsorbates consisted of seven to nine steps appropriately spaced to yield the type of Langmuir plot illustrated for ethane in Figure 3. It was possible to draw a very good straight line through the majority of points occurring at higher pressures. The two or three points at lower pressures were regarded as not obeying the Langmuir equation. However, a careful examination of several plots that

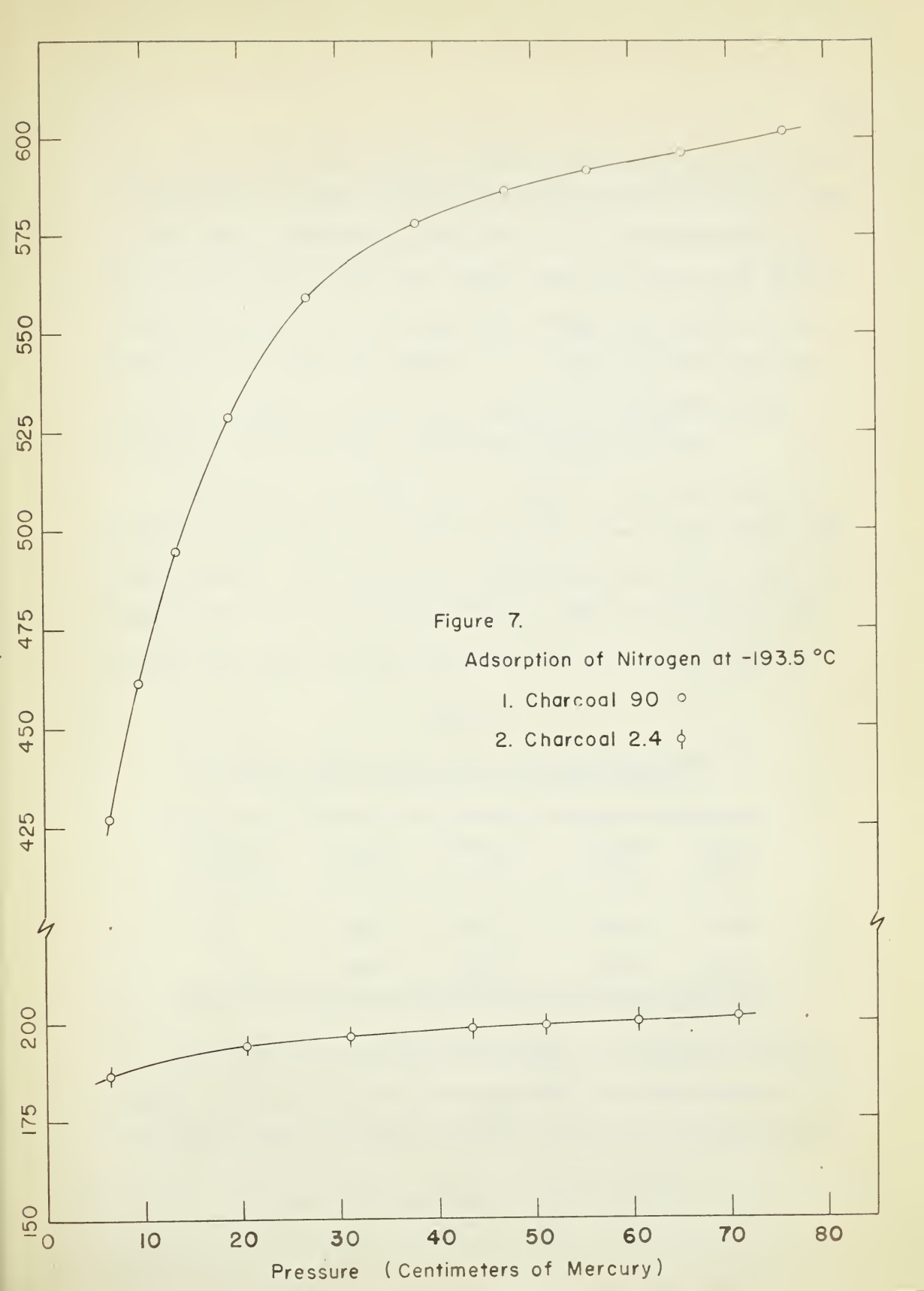


Figure 7.

Adsorption of Nitrogen at -193.5 °C

1. Charcoal 90 ○

2. Charcoal 2.4 ⊖

had a considerably larger number of points in this region revealed that it was possible to draw a straight line here in addition to the one that had been used to calculate V_m (Figure 8). As for the plots with only two or three points in the lower region, many were also seen to exhibit a second linearity, the line being drawn through these points and the first one on the other line (Figure 9). It may be that the two lines result from changes of state in the adsorbed film resembling those occurring in surface films of insoluble substances on water.

Calculations were made from the slopes of the lower lines for charcoals 2.4 and 60 to see how the monolayer volumes would compare with those in Table I. The results are listed in Table XI and are seen to be slightly lower than the values in Table I. With two exceptions, they are also less than the volumes adsorbed at 60 cm. pressure (Table X).

TABLE XI

MONOLAYER VOLUMES (ml.(n.t.p.)/g.) CALCULATED FROM THE SLOPE OF THE LANGMUIR PLOT AT LOWER PRESSURES

Charcoal Activity	Nitrogen -193°C	Acetylene -81°C	Ethylene -101°C	Ethane -86°C
60	354.4	292.9	249.0	218.8
2.4	200.0	153.1	136.7	115.2

In view of the foregoing observations, it is suggested that the Langmuir equation is not the most appropriate for interpretation of the data obtained here. In spite of this, it is felt that its use resulted

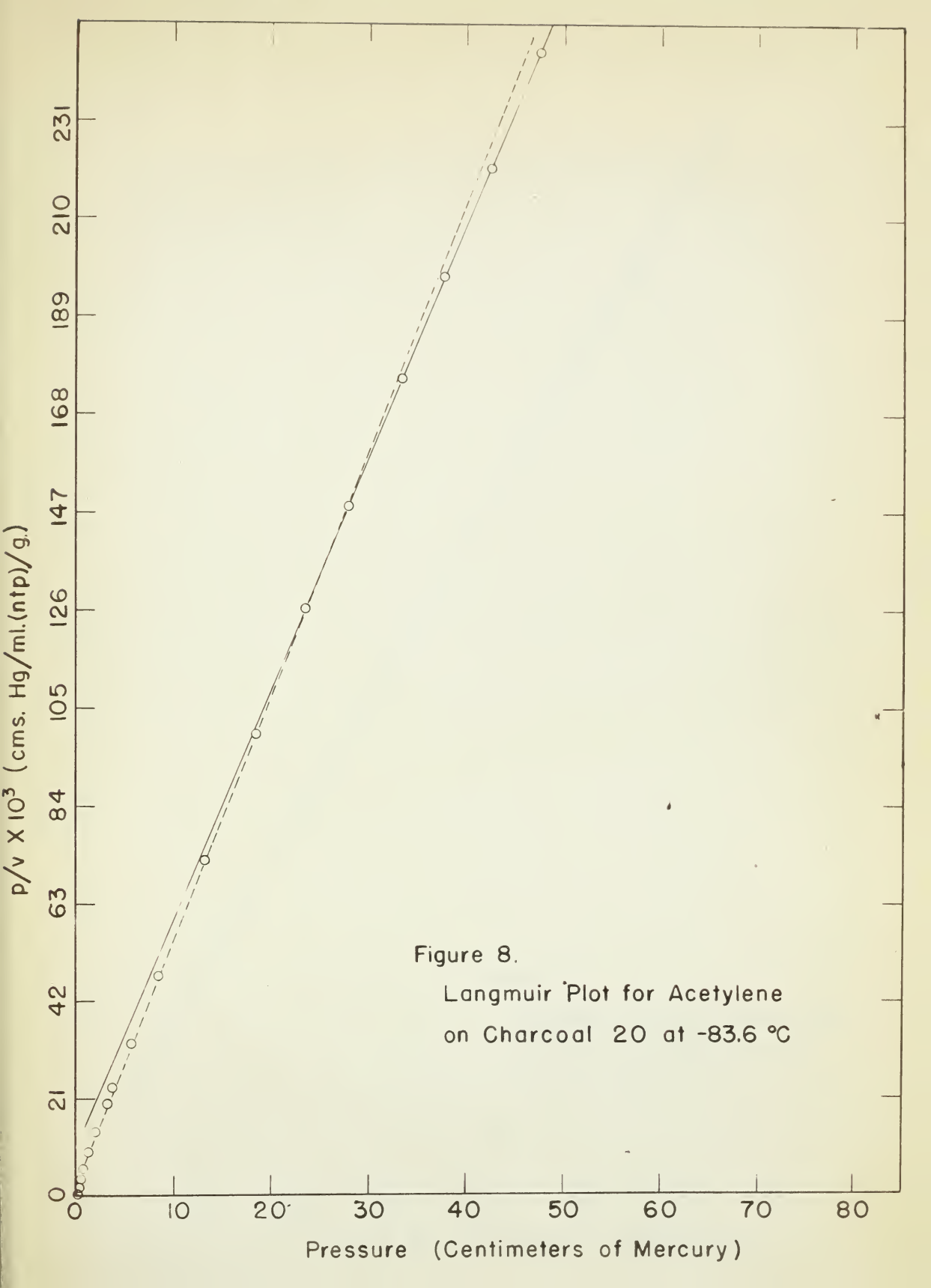


Figure 8.

Langmuir Plot for Acetylene on Charcoal 20 at -83.6 °C

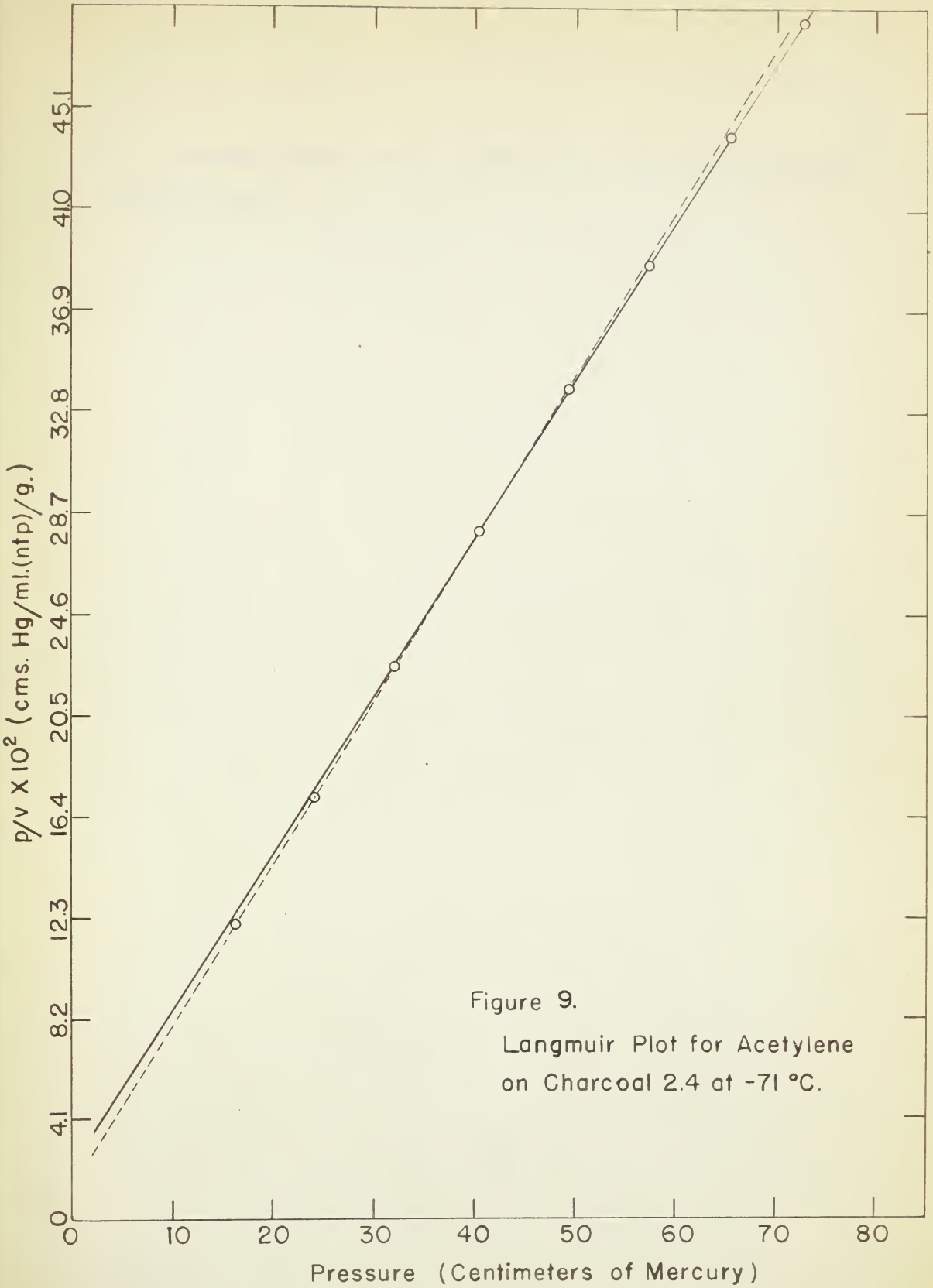


Figure 9.

Langmuir Plot for Acetylene on Charcoal 2.4 at -71 °C.

in a reasonable estimate of the charcoal surface areas and the molecular adsorption areas.

TABLE X

VOLUME (ml.(n.t.p.)/g.) ADSORBED AT 60 CENTIMETERS PRESSURE OF MERCURY

Charcoal Activity	Nitrogen		Acetylene		Ethylene		Ethane	
	-193.5	-182.5	-81	-71	-101	-91	-86	-76
90	594.8	504.4	466.3	430.6	410.0	386.3	365.0	344.3
60	365.5	330.0	282.4		250.0	236.5	219.9	
20	247.6	232.4	192.9	184.1*	172.0*	165.5*	149.2	145.8*
2.4	200.0	187.2	154.6	147.7	136.8	131.4	118.5	114.1
1.4	176.0	166.0	138.1		122.1		104.9	
				*-70°C	*-103°C	*-94°C		*-80°C

SUMMARY

The molecular adsorption areas of the hydrocarbon gases, acetylene, ethylene and ethane on coconut shell charcoal were estimated by a comparison of their V_m values with those of nitrogen.

The charcoal series used in this work did not exhibit any difference in sieving for the four gases. Consequently, the relative molecular adsorption thicknesses of the three hydrocarbons were not revealed.

Although the Langmuir equation did not apply over the entire range of pressures at which the isotherms were measured, the volumes calculated from the slopes of the Langmuir plots permitted a reasonable comparison of the charcoal surface areas and the molecular adsorption areas.

Calculations of the differential heats of adsorption of the four gases on extreme members of the charcoal series showed that the least activated members of the series exhibited a significantly higher affinity for the various gases.

Thus, the term "activity" is not synonymous with available surface area but should include the affinity of the surface for the adsorbate. For example, the adsorption of nitrogen at -40°C on charcoals 1.4, 2.4, 60 and 90 indicate that at this temperature, the surface affinity of the less activated charcoals more than compensates for their lower surface areas.

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